7/PRTS

# Proton Exchange Membrane Materials Based on Sulfonated Poly(phthalazinones)

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5    **BACKGROUND OF THE INVENTION**

In recent years, polymer electrolyte fuel cells have been identified as promising power sources for vehicular transportation and other applications requiring clean, quiet and efficient portable power. As a vital part of the fuel cell, proton

10    exchange membranes (PEM)s have become a rapidly growing area of research. Until now, PEMs have been mainly limited to perfluorinated ionomer membranes such as Nafion™ developed by DuPont and similar membranes commercialized by Dow and Asahi. In spite of their outstanding properties such as excellent proton conductivity and oxidative resistance, which are essential for fuel cell application, the

15    perfluorinated ionomer membranes are very expensive (US$800-2000/m$^2$) and suffer from other serious drawbacks of high methanol permeation and dehydration. In order to develop alternatives to Nafion™, which would be less expensive and free from other disadvantages of perfluorinated ionomer membranes, several attempts have been recently made including synthesis of new polymer electrolytes[1-5], chemical

20    modification of available high performance polymers[6-10], and blend membranes[11-14]. Among these studies, introducing sulfonic acid groups into the main chains of high performance polymers by sulfonation reaction is an important and widely used method for imparting polymers with proton exchange capability. Poly(aryl ether ketone)s, poly(phenylene oxide), poly(phenylene sulfide), poly(aryl ether sulfone),

25    and polybenzimidazole are among those that have been studied. The sulfonating agents include concentrated sulfuric acid, chlorosulfonic acid, pure or complex sulfur trioxide, and acetyl sulfate. As an example, the sulfonation reaction of Victrex™ PEEK and the conductivity of sulfonated PEEK have been studied extensively[7, 11, 15-17]. The DS could be controlled by reaction time and temperature in concentrated

30    sulfuric acid or oleum. For sulfonated PEEK with a relatively low DS of 0.65, its conductivity reaches 0.04 S cm$^{-1}$ at 100°C/100% RH, higher than that of Nafion-117 measured under the same conditions.

Poly(phthalazinone ether ketone) (PPEK) is one of a new class of poly(aryl
ether ketone)s under consideration for commercialization. PPEK has a very high glass
transition temperature of 263°C, excellent high-temperature stability, and many other
good properties. The sulfonation reactions of its copolymer, poly(phthalazinone ether
5    sulfone ketone) (PPESK), and the nanofiltration and ultrafiltration membrane
properties have also been studied[18-23].

## SUMMARY OF THE INVENTION

10        According to the invention, the sulfonation reaction of several
poly(pthalazinones) have been investigated, and suitable PEMs acquired from the
sulfonated products.

       According to one aspect of the invention, a series of sulfonated
15   poly(pthalazinone)ether ketones (PPEKs), (SPPEKs) with different DSs were
prepared via modification of PPEK with the mixture of concentrated sulfuric acid and
fuming sulfuric acid as the sulfonating agent. The structure and some properties of
SPPEKs and resulting membrane films were characterized, including: sulfonation
position, proton conductivity, equilibrium water uptake, swelling ratio and
20   thermostability as a function of DS.

       Similarly, a series of poly(pthalazinone) ether sulfone ketones(PPESKs), and
poly(pthalazinone) ether sulfones(PPESs) were prepared and tested.

## 25   BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic illustration of the synthetic pathway for SPPEK;
Figure 2 is a $^1$H-NMR spectrum of PPEK in CDCl$_3$;
Figure 3 is a $^1$H-NMR spectrum of SPPEK in DMSO-d$_6$;
30   Figure 4 is a $^{13}$C-NMR spectrum (hydrogen decoupled) of PPEK in CDCl$_3$;
Figure 5 is a FT-IR spectra of PPEK and SPPEK;
Figure 6 is a graph illustrating TGA traces of PPEK and SPPEKs;

Figure 7 is a graph illustrating the Conductivity of SPPEK;

Figure 8 is a graph of Conductivity versus temperature for SPPES and SPPESK; and

Figure 9 is a graph of Conductivity of SPPEKs of various DS.


5    DETAILED DESCRIPTION OF THE INVENTION


EXPERIMENTAL

**Materials**

PPEK was synthesized according to the procedure reported previously[18,19]. All other

10   chemicals obtained commercially were reagent grade and used as received.

**Sulfonation Reaction**

In a typical small-scale experiment, 0.5 g PPEK powder was added to a 10 mL

mixture of 95-98% concentrate sulfuric acid and 27-33% fuming sulfuric acid under

an argon atmosphere and the mixture was magnetically stirred at room temperature

15   (23°C) for a certain reaction time. The reported reaction time is the total time for

polymer dissolution and reaction. After a determined reaction time, the reaction

medium was poured onto crushed ice and the resulting precipitate was recovered by

filtration, washed with deionized water until the pH value was ~6-7.

For scaled-up reactions of 30-35 g, an ice bath was needed initially to cool the

20   heat released during dissolution. An amount of 30 g PPEK powder was added to a

mixture of 240 mL 95-98% concentrated sulfuric acid and 360 mL 27-33% fuming

sulfuric acid under an argon atmosphere and the mixture was magnetically stirred in

an ice bath. About 0.5 h later, the ice bath was removed and the stirring was continued

at room temperature (23°C). $^1$H-NMR was used to trace the DSs. After a determined

25   reaction time, the reaction medium was poured onto crushed ice and the resulting

precipitate was recovered by filtration, washed with deionized water until the pH

value was ~6-7.

**Polymer Analysis and Measurement**

Proton and carbon spectra were obtained on a Varian Unity Inova NMR spectrometer

30   operating at a proton frequency of 399.951 MHz and a carbon frequency of 100.578

MHz. Tetramethylsilane was used as the internal standard chemical shift reference.

$^1$H-NMR spectra of PPEK and low DS SPPEK were acquired at a temperature of

22°C in deuterated chloroform (CDCl₃). Deuterated methylene chloride ($CD_2Cl_2$)

was used when accurate integration values were desired for high field aromatic

signals since the signal of residual $CH_2Cl_2$ (5.31 ppm) did not interfere with the

aromatic region. Deuterated dimethylsulfoxide (DMSO-d₆) was the NMR solvent of

5    choice for higher DS SPPEK. Presaturation of the large water peak always present in

SPPEK at around 4 ppm improved the spectra by increasing the signal to noise ratio

and by removing interference signals from the large water absorption. $^{13}$C NMR

spectra of PPEK were acquired using a 10 mm tunable broadband probe and a

concentrated sample in CDCl₃ (500mg in 3mL). A quantitative spectrum was

10   obtained using long relaxation delay and hydrogen decoupling only during the

acquisition time. IR spectra were measured on a Nicolet 520 Fourier transform

spectrometer with powder samples inside a diamond cell.

A TA Instruments thermogravimetric analyser (TGA) instrument model 2950

was used for measuring the degradation temperatures ($T_d$ ) and a TA Instruments

15   differential scanning calorimeter (DSC) model 2920 calibrated with Tin at 231.93°C

and Zinc at 419.53°C was used for measuring the glass transition temperatures ($T_g$).

Polymer samples for TGA analysis were preheated to 150°C at 10°C/min under

nitrogen atmosphere, held isothermally for 60 min, equilibrated at 80°C, then heated

to 800°C at 10°C/min for $T_d$ measurement. Hence, the degradation data reported here

20   were assumed to be in the absence of moisture. Samples for DSC analysis were

initially heated at a rate of 10°C/min under nitrogen atmosphere to well below the

polymer $T_d$ point, quenched in liquid nitrogen and then re-heated at the same rate.

Inherent viscosities were determined using an Ubbelohde viscometer for N,N-

dimethylformamide solutions of polymer with a concentration of 0.5g/dL at 30°C.

**Preparation of Membrane Films**

An amount of 0.7 g sample was dissolved in 12 mL of $N,N$-dimethylformamide
(DMF) or $N,N$-dimethylacetamide (DMAc) and filtered. The filtered solution was
poured onto a glass plate and dried at 40°C for about two days. Residual solvent was

5       further evaporated at 120°C under vacuum for 48 h, resulting in yellow membrane
films.

**Water Uptake Content Measurement and Swelling Ratio**

All polymer membranes used were vacuum dried at 120°C before test. The sample
films were soaked in deionized water for different time at determined temperatures.

10      Weights of dry and wet membranes were measured. The water uptake content was
calculated by

$$\text{Uptake content } (\%) = \frac{\omega_{wet} - \omega_{dry}}{\omega_{dry}} \times 100\%$$

Where $\omega_{dry}$ and $\omega_{wet}$ are the masses of dried and wet samples respectively. The
swelling ratio was calculated from films 7~10 cm long by:

15      $$\text{Swelling ratio } (\%) = \frac{l_{wet} - l_{dry}}{l_{dry}} \times 100\%$$

Where $l_{dry}$ and $l_{wet}$ are the lengths of dry and wet samples respectively.

**Conductivity**

The proton conductivity was measured by AC impedance spectroscopy over a
frequency range of $1\text{-}10^7$ Hz with oscillating voltage 50-500 mV, using a system

20      based on a Solarton 1260 gain phase analyzer. A sample with diameter 10 mm was
placed in an open, temperature controlled cell, where it was clamped between two
blocking stainless steel electrodes with a permanent pressure of about 3 kg/cm$^2$.
Specimens were soaked in deionized water prior to the test. The conductivity ($\sigma$) of
the samples in the transverse direction was calculated from the impedance data, using

25      the relation $\sigma = d/RS$ where d and S are the thickness and face area of the sample
respectively and R was derived from the low intersect of the high frequency semi-
circle on a complex impedance plane with the Re (Z) axis.

**RESULTS AND DISCUSSION**

**Sulfonation reaction**

30      Figure 1 shows the sulfonation reaction, whereby sulfonation occurs as expected
around the electron-donating ether linkage.

In general, sulfonation of polymers can be conducted with several sulfonating agents, including concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid and acetyl sulfate, depending on the reactivity of the polymer. For Victrex PEEK, a high DS can be achieved with concentrated sulfuric acid because of the high reactivity

5    of the hydroquinone segment in the polymer chain. We initially attempted the sulfonation of PPEK in 95-98% concentrated sulfuric acid at both room and elevated temperatures. However, the results listed in Table 1 show that almost no sulfonation of PPEK took place at room temperature even for a very long reaction time, and only SPPEK with a very low DS was obtained at 60°C after 60 h. Sulfonation is an

10   electrophilic reaction affected by both the electrophilicity of the sulfonating agent and the electron donating characteristics of polymer. Compared with PEEK, PPEK (as shown in Fig. 1) has more electron-withdrawing functionality per repeat unit, which decreases the reactivity of the electron-donating ether linkage of the polymer. In order to prepare SPPEK with a high DS, 27-33% fuming sulfuric acid and elevated reaction

15   temperature were employed. As shown in Table 1, the sulfonation of PPEK in oleum at 40°C for 1 h resulted in SPPEK with a DS of 1.6. The DS didn't increase significantly over extended reaction times. This is because the sulfonic acid groups are more than 1.5 per repeating unit, reducing the electron-donating characteristic of the polymer and preventing the further introduction of more sulfonic acid groups.

20   Although a high DS was achieved using fuming sulfuric acid, the reaction proceeded too rapidly to maintain control. Abating the reaction to room temperature reduced the DS to 1.3. However, at a DS of 1.3, SPPEK is water soluble and can not be used as a PEM in fuel cell where high humidity exists. A further reduction in temperature made the PPEK solution in fuming sulfuric acid too viscous to completely dissolve the

25   polymer, which may result in a heterogeneous sulfonation reaction. In order to reduce the reactivity of the sulfonating agent, a mixture of 95-98% concentrated sulfuric acid and 27-33% fuming sulfuric acid was used for PPEK. As seen in Table 1, by varying the ratio of concentrated sulfuric acid to fuming sulfuric acid and the reaction time, the sulfonation reaction was more readily controlled to different DSs in the range of

30   0.6 to 1.23.

Table 1 Dependence of DS on the reaction conditions

| Oleum/ Concentrated sulfuric acid | Reaction temperature (°C) | Reaction time (h) | DS |
|---|---|---|---|
| 0/10 | R.T. | 95 | ~0 |
| - | 60 | 6 | <0.1 |
| 4/6 | R.T. | 4 | 0.1 |
| 5/5 | R.T. | 1 | 0.6 |
|  |  | 4 | 0.8 |
|  |  | 7 | 0.9 |
| 6/4 | R.T. | 1 | 0.8 |
|  |  | 4 | 1.0 |
|  |  | 7 | 1.1 |
| 7/3 | R.T. | 1 | 1.0 |
|  |  | 4 | 1.2 |
| 10/0 | R.T. | 1 | 1.3 |
|  | 40 | 1 | 1.6 |
|  |  | 2 | 1.6 |
|  |  | 23 | 1.7 |

Reaction conditions: PPEK 0.5 g, mixture of sulfuric acid 10 mL, argon atmosphere. R.T.: Room Temperature

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**NMR**

In order to determine the sulfonation site and the DS quantitatively, the $^1$H-

10    NMR spectra of PPEK in CDCl$_3$ (Figure 2) and SPPEK in DMSO-d$_6$ (Figure 3) were

characterized. The number system adopted for the protons in the polymer and the

derivatives are shown in Figure 2 to4. The careful and accurate assignments of NMR

spectral signals was essential for determining both the DS and the site of sulfonation.

The starting point for peak assignment of $^1$H and $^{13}$C-NMR of PPEK was from

the absorptions resulting from atoms surrounding the electron rich ether moiety. In a

PPEK repeat unit, the hydrogen atoms at the ortho position to the ether linkage are

more shielded than any other hydrogen atoms due to resonance effect of the oxygen

5      lone pair electrons. The other functional groups present in PPEK have a deshielding

effect on nearby nuclei. As a result of that, the furthest upfield signals (7.08-7.30

ppm) arise from the 4H ortho to the ether linkage. 2D COSY NMR as well as simple

homonuclear decoupling experiments showed the presence of two separate spin

coupling systems originating from these high field signals (Figure 2). These

10     interactions are a result of spin-spin coupling between the hydrogen atoms at the ortho

and meta positions of these phenol rings. One spin system consists of the high field

ortho ether 2H absorption at 7.16-7.30 ppm coupled with the distinct signal at 7.60-

7.72 ppm. The other spin system consists of the high field ortho ether 2H absorption

at 7.08-7.16 ppm coupled with the multiple absorptions at 7.76-8.06 ppm.

15     The results of a simple $^{13}$C-NMR experiment allowed formal assignment of

the preceding hydrogen signals, which are key components for the accurate

measurement of the DS of SPPEKs. The H-decoupled $^{13}$C-NMR spectrum of PPEK

is displayed in Figure 4. The carbon peaks of particular interest are the ones arising

from carbon atoms directly linked to an electron-withdrawing heteroatom (N or O)

20     causing absorptions to appear at lower field (144-195 ppm). The furthest downfield

signal (193.6-194.8 ppm) is unequivocally from the ketone carbon. Further upfield,

three carbon signals (155-162 ppm) arise from carbon atoms linked to electronegative

oxygen atoms in the phthalazinone and ether functionalities. Finally, the less

electronegative nitrogen atoms give the carbon absorptions at higher field (144-148

25     ppm). In one $^{13}$C-NMR experiment, a spectrum was acquired with decoupling of one

of the hydrogen frequencies (7.60-7.72 ppm) responsible for the 2H at the meta

position of one of the phenol rings. The resulting spectrum was compared with a $^{13}$C-

NMR spectrum acquired with full hydrogen coupling. Of all the downfield carbon

signals, the C-O absorption at 156.0-157.1 ppm and the C-N at 147.0-148.0 ppm both

5    lost a 6-7 Hz long range (3 bond C-C-C-H) carbon-hydrogen coupling when the

hydrogen frequency 7.60-7.72 ppm had been irradiated. Hence, the long-range C-H

interaction could *only* originate from C(O)-27 coupled with H-25,29 and C(N)-4

coupled with H-25,29. Decoupling of the other meta-ether hydrogen atoms H-19,23

would not affect any of the 2 C-N carbons. This experiment lead to the unequivocal

10   assignment of H-20,22 and H-26,28 which are essential for the DS calculations. The

assignment of H-25,29 and H-19,23 were also derived from this experiment. Further

1D and 2D heteronuclear (C and H) NMR experiments confirmed the previous

assignments. Table 2 and 3 list the chemical shift of the $^1$H and $^{13}$C-NMR spectra of

PPEK repectively.

15

Table 2  $^1$H-NMR data of PPEK in CDCl$_3$

| Proton Number | Chemical shift δ (ppm) | Integral intensity (number of H) |
|---|---|---|
| H-6,7,8,9,12,13,15,19,23 | 7.76-8.06 | 9H |
| H-16 | 8.54-8.68 | 1H |
| H-20,22 | 7.08-7.16 | 2H |
| H-25,29 | 7.60-7.72 | 2H |
| H-26,28 | 7.16-7.30 | 2H |

**Table 3**  $^{13}$C-NMR data of PPEK (hydrogen decoupled) in CDCl$_3$.

| Carbon Number | Chemical shift δ (ppm) |
|---|---|
| C-1 | 158.72 |
| C-4 | 147.0-148.0 |
| C-5-10,12-16,18,19,23-25,29 | 125.0-137.0 |
| C-11 | 144.8-146.0 |
| C-17 | 193.6-194.8 |
| C-20,22 | 117.6-118.6 |
| C-21 | 160.2-161.4 |
| C-26,28 | 119.4-120.4 |
| C27 | 156.0-157.1 |

The hydrogen absorption at low field (8.54-8.68 ppm) is strongly believed to arise from H-16 (Figure 2) although it could not be formally proved. The chemical shift position of many peaks in $^1$H and $^{13}$C-NMR spectra is seen to be not averaged out as would be the case where free rotation occurs. It is believed that PPEK is hindered by restricted rotation around certain linkages. In a "restricted" structure, H-16 would have an intensity of 1, as observed, and also would be in close proximity to the phthalazinone carbonyl. The proximity to the carbonyl would deshield H-16 more than any other hydrogen atoms nearby one of the carbonyl groups of PPEK.

**DS calculations from $^1$H-NMR:**

A $^1$H-NMR of PPEK in CD$_2$Cl$_2$ was acquired and the integration value of the upfield H-26,28 and H-20,22 absorptions was set to 4.00. The integration values of the other regions of the spectra corresponded exactly (table 2) to the number of hydrogen atoms expected from the chemical structure of PPEK repeat unit .

Similarly, in a quantitative $^{13}$C-NMR experiment, the upfield carbon signals C-26,28 and C-20,22 were also set to an intensity of 4.00 and the integration values of the other peaks again matched precisely. Sulfonated PPEK is only soluble in highly polar solvents and DMSO-$d_6$ was chosen to dissolve SPPEK. Spectra of SPPEK DS 1.03

5 and 1.63 are displayed in Figure 3. In comparison with PPEK, several new signals for the SPPEK derivatives appear with different chemical shifts due to the different solvents used and perturbation by different DSs of -SO$_3$H groups. The ortho-ether hydrogen atoms remained at high field but their intensity decreased as they were replaced by -SO$_3$H groups. More importantly, the ratio of low field H-16 (8.40-8.55)

10 ppm to multiple peaks 7.60-8.40 ppm (which do not include ortho-ether protons) always remained 1.00:11.00 for low and high sulfonation degrees. This is proof that substitution occurred only at the ortho-ether sites of the PPEK repeat unit. Another phenomenon supporting this is the variation in size of the small high-field signal at 7.30-7.40 ppm due to mono-substitution on SPPEK repeat units. When strong

15 electron withdrawing sulfonic acid groups are attached to benzene rings, they induce deshielding of hydrogen in the ortho and para positions. In monosubstituted SPPEK (DS~1), H-20 is deshielded by the -SO$_3$H group hence shifted downfield. In disubstituted SPEEK repeat units (DS>1), H-20 is still deshielded by the -SO$_3$H group present on the phenol ring but it is also shielded by the proximity through space

20 of the electron-rich oxygen atoms of the other -SO$_3$H group nearby on the other phenol ring. The DS was simply measured by presetting the integration value of the low field hydrogen absorptions to 12H (7.50-8.60 ppm) and determining the intensity value of the upfield hydrogen signals. This value represents the number of hydrogen atoms that have not been converted into -SO$_3$H groups and therefore substracting it

25 from 4H (unmodified PPEK) gives a direct DS value for SPPEK.

## FT-IR

Fourier Transform Infrared (FT-IR) Spectroscopy was used to confirm the pendant

5   SO$_3$H group on the polymer chain. Figure 5 shows the FT-IR spectra of parent PPEK

and its sulfonated derivatives with DSs of 1.03 and 1.63 respectively. In comparing

these spectra, one can see that in addition to the predicable absorptions at 3400 cm$^{-1}$

due to the stretching of the hydroxyls of SO$_3$H groups, the SPPEK absorption bands at

1020 and 1081 cm$^{-1}$ are characteristic of the aromatic SO$_3$H symmetric and

10  asymmetric stretching vibrations respectively. These two characteristic peaks increase

with higher DS. In addition, the reaction can be readily followed by the signal at 1500

cm$^{-1}$ related to 1,4-aromatic ring substitution. Introduction of SO$_3$H onto the aromatic

ring induces the formation of two new adsorptions at 1471 and 1475 cm$^{-1}$, which at

higher sulfonation degree, completely replace the adsorption at 1500 cm$^{-1}$. The

15  introduction of sulfonic acid groups in the modified polymer is thus confirmed.


## Thermal analysis

The thermal stabilities of the SPPEKs were determined by TGA. All the

samples were preheated at 150°C for 60 min in the TGA furnace to remove

20  moisture,then dynamic TGA experiments were run from 80 to 800°C at a heating rate

of 10°C/min under nitrogen. Figure 5 shows the degradation curves. The parent

PPEK is a thermostable polymer of which the 5 wt% loss temperature is nearly

500°C. For the sulfonated PPEK, there are two transitions of loss in weight. The first

one occurs at about 300°C and could be ascribed to the decomposition of the SO$_3$H

25  groups. In order to confirm our speculation, the weight loss from the initial point to

455°C of SPPEK with DS of 1.0 was analyzed. A value of about 15% was obtained,

which is close to the theoretical SO$_3$H weight loss percentage of 16% in SPPEK with

DS of 1.0. The second thermal degradation at about 490°C is assigned to the

degradation of the main polymer chain, which is in close agreement to the weight loss

step in the TGA curve for parent PPEK. In addition, SPPEKs with higher DS lose weight more quickly than those with lower DS, in the temperature range of 300 to 460°C. It also indicates that the weight loss during this period is due to the elimination of –SO$_3$H groups.

5

The $T_g$ of starting material is 263°C. For sulfonated product, only the $T_g$s of SPPEKs with DSs of 0.1 and 0.6 have been detected at 270°C and 292°C, respectively. The introduction of sulfonic groups into polymer chains leads to increased $T_g$s because of the increased intermolecular ionic interactions. For SPPEK

10    with DS higher than 0.6, no $T_g$s have been detected because the decomposition temperatures are lower than the $T_g$s.


**Solubility and Viscosity**

PPEK is soluble in CHCl$_3$, chlorobenzene and some other chlorinated solvents, but

15    insoluble in polar aprotic solvents such as $N,N$-dimethylformamide (DMF), $N,N$-dimethylacetamide (DMAc) and dimethylsulfoxide (DMSO). SPPEK with low DS, such as DS of 0.1 has similar solubility characteristics to the parent polymer. However, SPPEKs with high DSs are soluble in these dipolar aprotic solvents, but insoluble in chlorinated solvents. DMF was chosen as the solvent for determining the

20    inherent viscosities [η] of SPPEKs with high DS, which are listed in Table 4. It shows that the inherent viscosities of SPPEKs are higher compared with that of PPEK of 0.6 in chloroform and generally increase with increasing DS suggesting that the polymer chain is not degraded during sulfonation. Only SPPEK with DS of 1.63 which is obtained with 27-33% fuming sulfuric acid had a slightly reduced viscosity. A

25    significant increase in the viscosity may arise from two factors: one is that the introduction of sulfonic acid into polymer chain caused an overall increase in the polymer molecular weight; the other is that hydrogen bonding related to sulfonic acid groups increases the molecular forces. The slight decrease in the viscosity of SPPEK with DS of 1.63 may be caused by degradation taking place during the sulfonation

30    reaction in undiluted fuming sulfuric acid.

Table 4 Inherent viscosities of SPPEK

| DS | $[\eta]$ dL/g |
|---|---|
| 0 | [a] 0.6 |
| 0.6 | 1.40 |
| 0.8 | 1.81 |
| 1.0 | 1.83 |
| 1.2 | 1.99 |
| 1.6 | 1.88 |

Determination conditions: SPPEK 0.5 g/dL in DMF, 30°C.

5      [a] In chloroform

**Water uptake and swelling ratio**

Adequate hydration of membranes is critical to fuel cell application. Water assists in the transportation of protons from the anode to the cathode. If the electrolyte

10    membrane is too dry, its conductivity falls; on the other hand, excess water results in cathode flooding and morphological instability of membrane. The water uptake and swelling ratio of SPPEK membranes were determined by measuring the change in the mass and length before and after hydration. The results are listed in Table 5, which show that the water uptake of SPPEK increases with the DS at both room temperature

15    and elevated temperature. At 80°C, water uptake and swelling ratio of SPPEKs with lower DS reach equilibrium values quickly. However, water uptake and swelling ratio of SPPEK with DS $\geq 1$ increase with time and some samples were swollen or dissolved in water. The molecular structure of SPPEK is composed a hydrophobic backbone and hydrophilic sulfonic acid groups. Absorbed water acts also as

20    plasticizer, which promotes the phase separation. When the DS is are high enough, it becomes easy for the SPPEK chains to be separated by water and dissolved.

Table 5. Water uptake and swelling ratio of SPPEK

| | Room temperature | 80°C | | | |
| | 3 days | 2 h | | 24 h | |
| DS | Water uptake (%) | Water uptake (%) | Swelling ratio (%) | Water uptake (%) | Swelling ratio (%) |
|---|---|---|---|---|---|
| 0.1 | 6 | 14 | 2.4 | 14 | 2.4 |
| 0.6 | 15 | 16 | 3.6 | 16 | 3.6 |
| 0.8 | 19 | 21 | 6.4 | 22 | 6.4 |
| 1.0 | 19 | 44 | 12 | 63 | 20 |
| 1.2 | 32 | Swelling | Dissolved | — | — |
| 1.6 | 100 | Dissolved | — | — | — |

**Proton conductivity**

Prior to conductivity measurements, all membrane samples were soaked in water1 or 2 days for hydration. The effect of the DS on the conductivity of SPPEK is shown in Figure 6, which shows that the conductivity of SPPEK at room temperature increases with DS and reaches $2 \times 10^{-2}$ S/cm for SPPEK with DS of 1.2. This value is similar to Nafion 117, which shows conductivity of $3 \times 10^{-2}$ S/cm. Figure 7 also shows the influence of temperature on the conductivity for DS 1.0 and 1.2 SPPEKs. As can be seen, the conductivities of these two SPPEKs increase with increasing temperature up to 95°C and reach $4 \times 10^{-2}$ S/cm and $6 \times 10^{-2}$ S/cm, respectively. Conductivity of SPPEK with DS of 1.0 drops sharply after that, which is probably caused by the dehydration of membrane. Compared with Nafion 117, the drop in conductivity at 80°C occurs at a higher temperature for SPPEK.


**CONCLUSIONS**

A series of SPPEKs with different DS were prepared from PPEK with a mixtures of fuming and concentrated sulfuric acid as both the solvent and sulfonating agent. The Structure of SPPEK was confirmed by FT-IR and the DS of SPPEK was determined by $^1$H-NMR. As the DS of SPPEK increases, $T_d$ decreased and $T_g$ increased. Membrane films prepared from SPPEKs show a continuous increase in water uptake and swelling ratio with DS. Membranes prepared form SPPEK with DS of 1.0 and 1.2 show attractively high conductivity of $10^{-2}$ S/cm at both room temperature and elevated temperature.


Data for SPPES and SPPESK prepared by sulfonating PPES and SPPESK respectively


**Sulfonation Reaction of SPPES**

An amount of 2 g PPES powder was added to a mixture of 16 mL 95-98% concentrated sulfuric acid and 24 mL 27-33% fuming sulfuric acid under an argon atmosphere and the mixture was magnetically stirred in an ice bath. About 15 min later, the ice bath was removed and the stirring was continued at room temperature (23°C). $^1$H-NMR was used to trace the DSs. After a determined reaction time, the

reaction medium was poured onto crushed ice and the resulting precipitate was recovered by filtration, washed with deionized water until the pH value was ~6-7.

## Sulfonation Reaction of SPPESK

An amount of 2 g PPESK powder was added to a mixture of 16 mL 95-98% concentrated sulfuric acid and 24 mL 27-33% fuming sulfuric acid under an argon atmosphere and the mixture was magnetically stirred in an ice bath. About 15 min later, the ice bath was removed and the stirring was continued at room temperature (23°C). $^1$H-NMR was used to trace the DSs. After a determined reaction time, the reaction medium was poured onto crushed ice and the resulting precipitate was recovered by filtration, washed with deionized water until the pH value was ~6-7.

## Conductivity

Prior to conductivity measurements, all membrane samples were soaked in water 1 or 2 days for hydration. Figure 8 shows the influence of temperature on the conductivity for SPPES and SPPESK with DS 1.0. As can be seen, the conductivity of SPPESK increases with increasing temperature up to 95°C and reaches $2 \times 10^{-2}$ S/cm, then drops sharply after that, which is probably caused by the dehydration of membrane. The conductivity of SPPES increases with increasing temperature up to 106°C and reaches $4 \times 10^{-2}$ S/cm, then drops Compared with Nafion 117, the drop in conductivity at 80°C occurs at a higher temperature for SPPEK.

## Proton conductivity

Prior to conductivity measurements, all membrane samples were soaked in water 1 or 2 days for hydration. The effect of the DS on the conductivity of SPPEK is shown in Figure 9, which shows that the conductivity of SPPEK at room temperature increases with DS and reaches $2 \times 10^{-2}$ S/cm for SPPEK with DS of 1.2. This value is similar to Nafion 117, which shows conductivity of $3 \times 10^{-2}$ S/cm. Figure 9 also shows the influence of temperature on the conductivity for DS 1.0 and 1.2 SPPEKs. As can be seen, the conductivities of these two SPPEKs increase with increasing temperature up to 95°C and reach $4 \times 10^{-2}$ S/cm and $6 \times 10^{-2}$ S/cm, respectively. Conductivity of SPPEK with DS of 1.0 drops sharply after that, which is probably caused by the dehydration of membrane. Compared with Nafion 117, the drop in conductivity at 80°C occurs at a higher temperature for SPPEK.

## Data for SPPEK prepared by polymerization of sulfonated monomers

*(This demonstrates that there are alternative methods of producing poly(phthalazinones)*

The random sufonated poly(phthalzinone ethers) have also been obtained via direct

polymerization reactions with the sulfonation sites on the deactivated aromatic rings

as depicted in scheme 1.

**Polymerization Reaction**

The SPPEKs synthesized with various compositions are denoted as SPPEK-n, where

n means the percentage content of SDFK in feed of DFK and SDFK. The synthesis of

SPPEK-50 is used as a typical example. To a three-neck flask with a magnetic stirrer,

a Dean-Stark trap and condenser, and an Argon inlet, 1.102 g DFK (5.05 mmol),

2.133 g SDFK-Na (5.05 mmol), 2.383 g DHPZ (10 mmol), and 1.8 g potassium

carbonate (13 mmol) were added. Then 18 mL of NMP and 25 mL chlorobenzene

were charged into the reaction flask under an argon atmosphere. The reaction mixture

was heated to 140°C. Upon dehydration and removal of chlorobenzene, the reaction

temperature was increased to 170-175°C. After a period of 5-7 h, when the solution

viscosity had obviously increased, several milliliters of NMP was added to dilute the

solution and kept it for further 3-5 h. Then, the mixture was cooled to 100°C and

coagulated in ethanol, water or acetone. After recovering and drying the product,

SPPEKs were purified by dialysis for 7 days, using a membrane-cellulose dialysis

tube (SPECTRUM) with a molecular weight cut off value of 3500.

**Preparation of Membrane Films**

An amount of 1 g SPPEK in sodium form was dissolved in 12 mL of *N,N*-dimethylacetamide (DMAc) and filtered. The filtered solution was poured onto a glass plate and dried at 40°C for about two days. Residue solvent was further evaporated at 120°C under vacuum for 48 h. resulting in yellow membrane films. The acid form membrane films were obtained by doping the sodium form membrane films into 2 N $H_2SO_4$ for 48 h, followed by doping in deionized water for 48 h, and vacuum drying at 100°C for 24 h.

**Scheme 1 Synthetic formula for SPPEK**
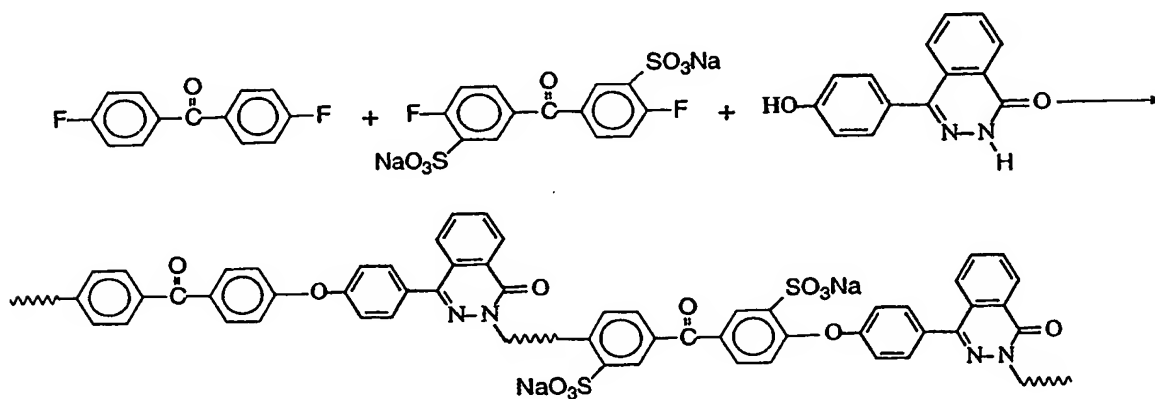
**Scheme 2 Preparing H-form membranes**



2N $H_2SO_4$
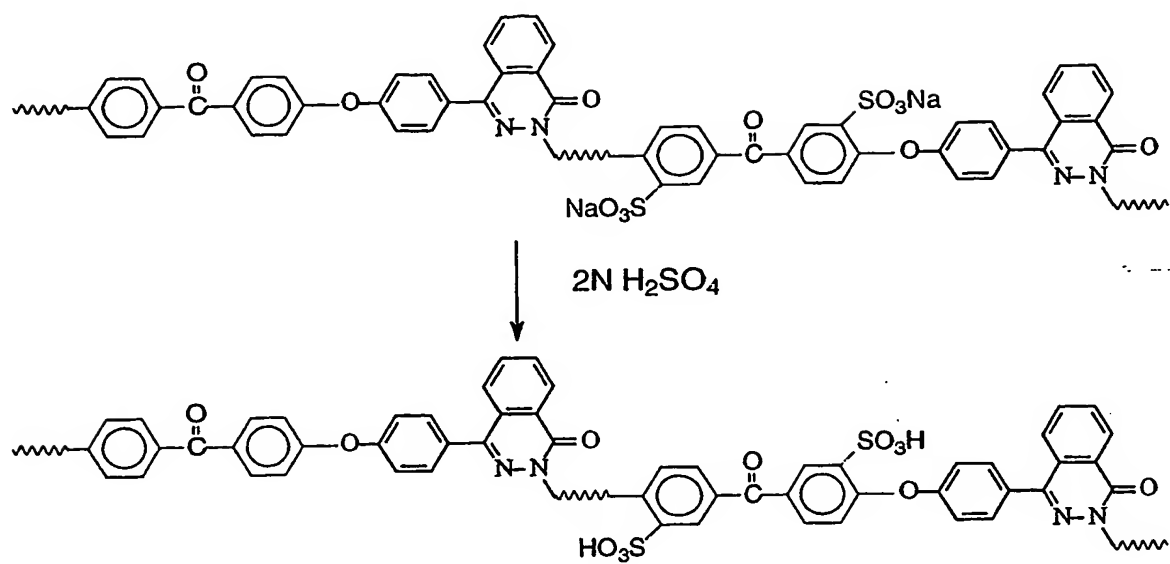
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